

Torrefaction and low-temperature carbonization of woody biomass: Evaluation of fuel characteristics of the products

Sang-Woo Park^{a,*}, Cheol-Hyeon Jang^a, Kyung-Ryul Baek^b, Jae-Kyung Yang^b

^a Department of Environmental Engineering, Hanbat National University, San 16-1 Duckmyung-dong Yusung-gu, Daejeon 305-719, Republic of Korea

^b Department of Environmental Engineering & Health Science, Cheongyang Provincial College, Cheongyang, Chungnam 345-702, Republic of Korea

ARTICLE INFO

Article history:

Received 27 February 2012

Received in revised form

6 July 2012

Accepted 10 July 2012

Available online 9 August 2012

Keywords:

Woody biomass

Thermal treatment

Torrefaction

Carbonization

Combustion characteristics

ABSTRACT

Preprocessing of woody biomass was performed with torrefaction and low-temperature carbonization. In this study, the pretreated samples have been used to evaluate the energy yield and fuel characteristics. The combustion profiles of the torrefied sample and the low-temperature carbonized sample blended with coal were examined in order to analyze the characteristics of co-combustion. Energy yields of 80–98% in torrefied samples and 46–63% in low-temperature carbonized samples were observed. It was found that in the low-temperature carbonization zone, the coal band moved toward that of coal. The number of differential thermogravimetric peaks decreased from two to one with an increase in the thermal-treatment temperature. In the case of samples blended with coal and low-temperature carbonized samples at 350 °C, it has been confirmed that the activation energy and all index parameters decreased as the blend ratio increased. It was confirmed that as a result, the combustion rate ($d\alpha/dt$) became higher owing to an increased value of the constant (k), which represents the reaction rate. However, in the case of the sample torrefied at 275 °C, it was confirmed that the combustion rate was not the same, according to the co-combustion ratio, because of an opposite tendency shown in the devolatilization and char combustion stages.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

In order to increase the energy recovery efficiency for woody biomass, several studies on co-combustion by blend biomass with coal have been conducted. However, many issues with respect to economic feasibility and fuel characteristics need to be resolved. The major issues are that the cost for collection and transportation is high and the grindability is poor. Another issue is that the combustion characteristics of woody biomass are different from those of coal due to its highly volatile components [1–3].

In order to address these shortcomings, torrefaction [4] has been proposed as a method of preprocessing biomass. Various studies on torrefied biomass have been carried out, focusing on energy balance [5], grindability improvement [6,7], and fuel characteristics [7–10]. It has been shown that the energy balance and grindability are improved through torrefaction. This is because the dehydration and decarboxylation reactions are carried out during the process of torrefaction. But, the fuel characteristics do not seem to be improved. The reason is that torrefaction is performed at low temperatures in the range 200–300 °C (reducing atmosphere). This

is because cellulose and lignin in woody biomass are decomposed at temperatures above 300 °C [11]. However, the reason that the thermal treatment is carried out in the low-temperature zone is to optimize the energy balance and to promote grindability.

Sahu et al. [12] determined the combustion characteristics of a coal-blended sample by pyrolyzing sawdust and rice husks at 300 °C and 450 °C. The IT of unprocessed samples (sawdust and rice husks) was found to be 243 °C and 251.7 °C, respectively. In the case of thermal decomposition at 300 °C, it was found to be 298.3 °C and 285.5 °C, respectively. In the case of thermal decomposition at 450 °C, it was found to be 356.6 °C and 330.7 °C, respectively. As a result, I could confirm that the combustion characteristics were improved because of thermal decomposition, taking into consideration that the IT of coal was 359.2 °C.

Abdullah and Wu [13] assessed the grindability and energy balance by pyrolyzing mallee wood in the temperature range 300–500 °C. Studies on samples pyrolyzed in the low-temperature zone, including torrefied samples, are ongoing to enhance the energy recovery efficiency of woody biomass. However, there are no studies on the fuel characteristics of the products of torrefaction or pyrolysis in the low-temperature zone.

In this study, the fuel characteristics of samples of torrefied woody biomass and of woody biomass thermally treated at

* Corresponding author. Tel.: +82 428211463; fax: +82 428211476.

E-mail addresses: bigsw21@gmail.com, bigsw21@hanbat.ac.kr (S.-W. Park).

Nomenclature

A	pre-exponential factor, s^{-1}
DTG_{max}	maximum weight loss rate, $\% s^{-1}$
E	activation energy, $kcal\ mol^{-1}$
$g(\alpha)$	integral function of conversion
w_f	final mass of the sample, mg
w_o	initial mass of the sample, mg
w_t	mass of the sample at time t , mg
α	conversion
β	heating rate, $^{\circ}C\ min^{-1}$
η_E	energy yield, %
η_M	mass yield, %
BT	burnout temperature, $^{\circ}C$
CW	carbonized wood chip
daf	dry ash-free basis
db	dry basis
DTG	differential thermogravimetric

FC	fixed carbon
FR	fuel ratio
GCV	gross calorific value, $kcal\ kg^{-1}$
GCV_t	gross calorific value of pyrolysis samples (dry basis), $kcal\ kg^{-1}$
GCV_u	gross calorific value of unprocessed samples (dry basis), $kcal\ kg^{-1}$
IT	initial temperature, $^{\circ}C$
OM	optimum mechanism
PT	peak temperature, $^{\circ}C$
R	gas constant, $8.314\ J\ K^{-1}\ mol^{-1}$
T	absolute temperature, K
TG	thermogravimetric
TW	torrefied wood chip
VM	volatile matter
WC	wood chip
W_t	mass after pyrolysis (at pyrolysis time t), g
W_o	mass before pyrolysis, g

temperatures in the range 300–400 $^{\circ}C$ (hereafter referred to as low-temperature carbonization) have been investigated. In order to evaluate the fuel characteristics, the energy yield and basic properties (ultimate analysis, proximate analysis, and calorific value), fuel ratio, coal band, and FT-IR spectra were examined. Furthermore, the combustion profile was elucidated by TG analysis, which was performed for products of torrefaction and low-temperature carbonization and for the coal-blended sample. The activation energy of the combustion profile was evaluated through the DTG characteristics and the combustion parameter.

In particular, we can predict the co-combustion of blended coal and biomass through combustion characteristics and rate analysis. For this, it is important to investigate all index parameters [12,14,15].

2. Experimental

2.1. Material and thermal-treatment conditions

Woody biomass was prepared by crushing pitch pine to 10–20 mm (thickness: 3 mm) and drying it at 70 $^{\circ}C$ (hereafter referred as WC Raw). Bituminous coal (Ensham mine, Australia) was used as the coal. The temperature for the thermal treatment was selected considering the grindability and economic feasibility. It is known that the grindability of wood torrefied below 250 $^{\circ}C$ is poor [4]. Therefore, the three temperatures of 250, 270, and 300 $^{\circ}C$ were selected for torrefaction. For low-temperature carbonization, the three temperatures of 325, 350, and 375 $^{\circ}C$ were selected, taking into account the energy yield and economic feasibility of the conditions for decomposition of the wood component. WC raw (10 g) was put into a crucible and the cover was closed to block the inflow of air, and the crucible (capacity: 80 cm^3) was then put in an electric furnace and pyrolyzed for 30 min [13,16]. After pyrolysis, the air-cooled samples were labelled TW250, TW275, and TW300 for torrefaction and CW325, CW350, and CW375 for low-temperature carbonization, according to the thermal-treatment temperature.

2.2. Energy yield and fuel characteristics

2.2.1. Energy yield

The mass yield and energy yield obtained when different temperatures and durations of pyrolysis were applied to WC were determined as follows:

$$\eta_M = \left(\frac{W_t}{W_o} \right) \text{ dry basis} \quad (1)$$

$$\eta_E = \eta_M \left(\frac{GCV_t}{GCV_u} \right) \text{ dry basis} \quad (2)$$

2.2.2. Fuel characteristics

Ultimate analysis was performed by measuring C, H, N, and S with an ultimate analyzer (Thermo 1112). Proximate analysis was performed in accordance with ASTM D3172 [17], D3174 [18], and D3175 [19]. Calorific values were measured with a calorimeter (Parr 1261 EA). All experimental runs were conducted three times and averaged to compensate experimental reproducibility. Fuel ratio is a characteristic value representing the properties of a solid fuel and is indicated as a ratio (FC/VM air-dried basis) of volatile matter against fixed carbon. The VM content was indicated on a dry, ash-free basis, based on the results of the proximate analysis. The coal-band is an index which assigns a coal rank based on the degree of coalification; it was investigated using a van Kravellen diagram [8] to plot the relationships between the atomic ratios H/C and O/C from the ultimate analysis.

For the specific surface area, the adsorption isotherm was measured using N_2 as the adsorbate gas, varying the gas pressure over the range 8–760 mm Hg and at a temperature of 77.35 K, using a surface area and porosity analyzer (TriStar II 3020, Micromeritics). Results were calculated using the Brunauer–Emmett–Teller (BET) isotherm.

2.3. Non-isothermal thermogravimetric analysis

TG analysis was conducted (TGA851e Mettler-Toledo) in an oxidation (air, 75 $mL\ min^{-1}$) atmosphere. The combustion profile was obtained by heating at a rate of 10 $^{\circ}C\ min^{-1}$ up to 800 $^{\circ}C$. The biomass was ground and the particles passed through a 100-mesh filter, and 10-mg sample were used. A DTG curve, indicating rate of weight loss with increasing temperature, was prepared to determine the combustion characteristics of raw biomass, char, coal, and biomass/coal blend. On the DTG curve, the initial temperature is the temperature at which the rate of weight loss as a result of evaporation of water reaches 0.01% s^{-1} , and the peak temperature is the point where the rate of weight loss is at its maximum. The burnout temperature is the point at which the rate of weight loss decreases to 0.01% s^{-1} .

The maximum weight loss rate at PT of the DTG curve was set as DTG_{max}. In the event that there were two DTG peaks between IT and BT, the first peak section was defined as the devolatilization stage (1st stage) and the second peak section as the lignin and char combustion stage (2nd stage) [20]. The reason we divide the process into two stages is that in the case of co-combustion of blended coal and biomass, the combustion characteristics are not the same. In general, coal shows uniform combustion characteristics, whereas in the case of biomass, the flames are unstable and the IT decreases owing to a lot of VM [14]. Accordingly, it is required to deduce the parameters necessary for combustion control after investigating the combustion characteristics for each stage through TG analysis before co-combustion. As far as the preparation of the blends is concerned, the total amount of blended coal and biomass was based on a standard amount of 4 g. From this amount, 10 mg were used for TG analysis. In general, TG analysis is based on a standard amount of 10 mg.

2.4. Kinetic parameters

The Coats–Redfern model, was used for calculating the kinetic parameters of the co-combustion of biomass char and coal. The theory for the calculation of kinetic parameters by the Coats–Redfern model [21] is as follows.

A two-stage reaction kinetics scheme consisting of two independent reactions is proposed for the thermal decomposition of the biomass under an oxidative atmosphere, represented by the DTG curves. The kinetic scheme includes two separate reactions:

A (raw material) → B (intermediate) + C1 (gas) (first stage)

B (intermediate) → C2 (gas) + D (ash) (second stage)

The approach used in the present work [20,22] to calculate the kinetic parameters was based on the Arrhenius equation, which has been used by several researchers to obtain the kinetic parameters of thermal events under combustion conditions.

These two separate reactions are thought to be governed by the first-order Arrhenius law, and so the kinetics of the reaction is described as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3)$$

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where $f(\alpha)$ represents the hypothetical model of the reaction mechanism, k is the reaction rate, A the pre-exponential factor (s^{-1}), E the activation energy ($kJ mol^{-1}$), R the gas constant ($8.314 J K^{-1} mol^{-1}$), T the absolute temperature (K), t the time (s) and α the loss in mass fraction or mass conversion ratio, which can be calculated by the following relationship:

$$\alpha = \frac{(w_0 - w_t)}{(w_0 - w_f)} \quad (5)$$

where w_0 is the initial mass of the sample, w_t is the mass of the sample at time t , and w_f is the final mass of the sample.

For a constant heating rate β ($^{\circ}C min^{-1}$) during combustion, $\beta = dT/dt$, Eq. (3) can be transformed into

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{k}{\beta}\right) dT \quad (6)$$

Integrating Eq. (6) gives

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

where $g(\alpha)$ is the integral function of conversion. If $E/(RT)$ is replaced by x and integration limits transformed, Eq. (7) becomes

$$g(\alpha) = \frac{AE}{RT} \int_x^{\infty} \frac{\exp(-x)}{x^2} dx \quad (8)$$

Eq. (8) can be written as

$$g(\alpha) = \frac{AE}{RT} P(x) \quad (9)$$

$p(x)$ has no analytical solution but has many approximations [23,24], with one of the most popular being the Coats–Redfern model. This method utilizes the asymptotic series expansion for approximating the exponential integral in Eq. (9), giving

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (10)$$

Since it can be demonstrated that for most values of E and for the temperature range of combustion, the expression $\ln[AR/\beta E(1 - 2RT/E)]$ in Eq. (10) is essentially constant, if $\ln[g(\alpha)/T^2]$ is plotted versus $1/T$, a straight line should be obtained. Moreover, if the correct $g(\alpha)$ is used, the plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line with a high correlation coefficient of linear regression analysis, from which the values of E and A can be derived. The activation energy E can be calculated from the slope of the line E/R , and by taking the temperature at which $w_t = (w_0 + w_f)/2$ as the intercept term of Eq. (10), the pre-exponential factor A can also be calculated.

The function $g(\alpha)$ or $f(\alpha)$ depends on the mechanism controlling the reaction and the size and shape of the reacting particles.

Table 1 shows the expressions of $g(\alpha)$ for the basic model functions usually employed for the kinetic study of solid-state reactions. By means of these functions, it was possible to estimate the reaction mechanisms governing the process of thermal oxidation of the samples from the TG curves. The form of $g(\alpha)$ that gives a straight line with the highest correlation coefficient will be

Table 1
Expressions of $g(\alpha)$ for the kinetic model functions usually employed for solid-state reactions [3,20,25].

Mechanism	Symbol	$g(\alpha)$
Chemical reaction		
First-order	O1	$-\ln(1 - \alpha)$
Second-order	O2	$(1 - \alpha)^{-1}$
Third-order	O3	$[(1 - \alpha)^{-2}]$
Limiting surface reaction between both phases		
Two dimensions	R2	$1 - (1 - \alpha)^{1/2}$
Three dimensions	R3	$1 - (1 - \alpha)^{1/3}$
Diffusion		
One-way transport	D1	α^2
Two-way transport	D2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
Three-way transport	D3	$[1 - (1 - \alpha)^{1/3}]^2$
Ginstling–Brounshtein equation	D4	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$

considered the function of the model that best represents the kinetics of mass loss for each separate reaction. In most dynamic studies that use TGA, the first-order chemical reaction assumption (O1 model) is the most frequently used. In addition to this reaction mechanism, other chemical reactions (O2 and O3 models), boundary controlled reactions (R2 and R3 models) and diffusion mechanisms (D1, D2, D3 and D4 models) are commonly applied to describe the combustion reactions of raw biomass, thermally treated woody biomass, coal, and thermally treated woody biomass/coal blend.

3. Results and discussion

3.1. Energy yields

As shown in Fig. 1, the mass yield and energy yield of the torrefied samples were higher than those of the low-temperature carbonized samples. It shows that the energy yield was higher than the mass yield in all samples, and the differences were greater in the low-temperature carbonized samples. This is because in the temperature zone for low-temperature carbonization, cellulose, which is a major component of wood, is devolatilized, increasing the fixed carbon.

It is known that the pyrolysis of wood components starts at temperatures in the range 160–200 °C for hemicellulose, 240–350 °C for cellulose, and 280–500 °C for lignin, and they release decomposition products such as CO, CO₂, and H₂O [26]. The conditions for TW275 among the torrefied samples produced the highest energy yield of 98%, more than twice the yield of 45% for CW375 among the low-temperature carbonized samples. The energy yields of the torrefied samples lie in the range 80–98%, depending on the temperature conditions, and those of the low-temperature carbonized samples in the range 45–63%. It has been demonstrated that the torrefied samples are superior with respect to energy yield [4].

3.2. Fuel characteristics

3.2.1. Basic properties

The physicochemical properties of the samples prepared at different thermal-treatment temperatures are summarized in Table 2.

As listed in Table 2, the calorific value of coal is 6385 kcal kg⁻¹, which is 1.45 times higher than the calorific value (4407 kcal kg⁻¹) of the unprocessed sample (Raw).

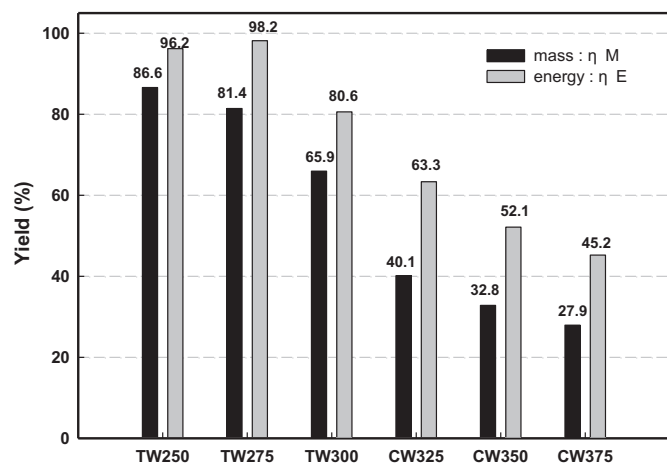


Fig. 1. Mass and energy yields.

However, the calorific value was shown to increase because of torrefaction and low-temperature carbonization. In particular, a rapid increase was observed in the low-temperature carbonized samples, which was because the temperature zone for thermal treatment expedited dehydration and devolatilization. In the result from industrial analysis, the above sample also showed increased FC and decreased VM compared to an unprocessed sample, which is a typical result for thermal treatment. It was confirmed that the fuel ratio becomes higher because FC shows a higher value than that of VM in the low-temperature carbonized samples.

The relationships between calorific values and VM (daf basis) and between calorific values and fuel ratios are shown in Fig. 2.

As shown in both Fig. 2a and Table 2a, the relationship between the calorific value and VM shows opposite trends to one another. In the zone of torrefaction, it was confirmed that as the temperature of thermal treatment rose, a reduction of VM and increase of calorific value were clearly shown. On the contrary, in the zone of low-temperature carbonization, the reduction of VM and increase of calorific value were not as strong.

This means that further VM reduction slowed down in the temperature range 325–375 °C, which was the zone condition for low-temperature carbonization. The temperature at which a distinct VM reduction and increase in calorific value was observed was between 300 and 325 °C. This is because in this zone, hemicellulose and cellulose components are actively decomposed.

Fig. 2b and Table 2a shows the variation in the calorific value and fuel ratio with the thermal-treatment temperature, and a similar pattern was observed for all samples, except for the CW325 and CW375 sample. It was observed that as the thermal-treatment temperature went up, the fuel ratio increased, and the calorific value increased as the fuel ratio neared 1.0, but the rate of increase slowed when the fuel ratio was above 1.0. As a result, the calorific value per specific weight varied depending on the VM content, and a higher calorific value was obtained as the fuel ratio neared 1.0.

3.2.2. Coal band

As shown in Fig. 3, it was observed that the coal-band characteristics of the samples moved toward those of coal at higher thermal-treatment temperatures. This was caused by devolatilization (decarboxylation, dehydrogenation) during the thermal-treatment process. Among the torrefied samples, TW250 and TW275 showed similar results to those for the beech wood torrefied at temperatures in the range 220–280 °C by Prins et al. [27]. It was found that the coal-band characteristics moved toward those of coal, as compared to those of the unprocessed sample, but they were still within the biomass zone.

On the other hand, those of the low-temperature carbonized samples showed bigger variations, as compared to those of the unprocessed sample or the torrefied samples. Furthermore, the torrefied samples showed a wide distribution range over the temperature range (250–300 °C), while the low-temperature carbonized samples displayed a concentrated distribution. TW300 and CW325 exhibited large variations even though the difference in temperature was only 25 °C. The results are very similar to those obtained in a previous study on mallee wood [13]. It was verified that in this temperature zone, decomposition occurred most actively, as mentioned previously.

3.2.3. FT-IR spectra

The variances in the FT-IR absorbance peaks for the torrefied samples (Fig. 4a) and the low-temperature carbonized samples (Fig. 4b) were measured. In the absorbance peak zone corresponding to the wave number range 3300–3500 cm⁻¹, the absorbance peaks for torrefied samples were similar to those for the unprocessed sample. However, the absorbance peak for the

Table 2
Physical and chemical properties of the thermally treated biomass and coal.

Sample	Proximate analysis (wt.%, adb)				Ultimate analysis (wt.%, db)					GCV (kcal kg ⁻¹ , db)	S _{BET} (m ² g ⁻¹)
	M	FC	VM	Ash	C	H	O ^{differ.}	N	S		
Coal	6.67	54.50	27.25	11.58	74.12	4.22	6.93	1.91	0.41	6385	11.86
WC raw	3.81	7.42	88.72	0.05	46.73	6.46	46.35	0.41	ND	4407	–
TW250	3.19	15.51	81.19	0.11	52.22	5.18	41.94	0.55	ND	4895	–
TW275	2.90	23.46	73.47	0.17	57.33	4.95	37.17	0.37	ND	5314	<1.0
TW300	2.81	29.36	67.58	0.25	59.03	4.78	35.59	0.34	ND	5387	–
CW325	3.29	51.57	44.71	0.43	68.43	4.31	26.47	0.35	ND	6956	–
CW350	3.40	52.56	43.57	0.47	69.20	4.28	25.71	0.32	ND	6998	<1.0
CW375	4.03	61.36	34.13	0.48	71.39	3.80	24.00	0.31	ND	7140	–

adb, Air-dried basis; db, dry basis; M, Moisture; O^{differ.}, by difference [(FC + VM)db – (C + H + N + S)db]; ND, not detected; S_{BET}, specific surface area determined on N₂ isotherms by the BET method.

low-temperature carbonized samples showed the opposite trend to that for the unprocessed sample. It is assumed that this is because of OH being dehydrated. In addition, it was observed that aliphatic CH₃ and CH₂, having absorbance bands corresponding to wave numbers in the range 2850–2920 cm⁻¹, were lower for the torrefied samples than for the low-temperature carbonized samples. It is assumed that this is because of the devolatilization caused by the thermal treatment. In order to see the images of the spectra in the range 1700–700 cm⁻¹ more clearly, I have magnified it. The results are shown in Fig. 4c and d.

It was shown that the C–O–C band was distributed widely over the wave number range 1600–1650 cm⁻¹ for the unprocessed sample, while it increased sharply at 1600 cm⁻¹ for the torrefied samples and the low-temperature carbonized samples. The peak at 1600 cm⁻¹ corresponds to an aromatic-ring vibration combined with oxygen in quinone, ether, or a heterocyclic compound [28]. The peak at 1370 cm⁻¹ corresponds to a methyl band, and it was observed that its intensity increased greatly for the torrefied samples and the low-temperature carbonized samples, as compared to that for the unprocessed sample. The peaks observed at wave numbers in the range 1200–1240 cm⁻¹ correspond to a C–O–C band; the absorbance band in this range increased for all samples, both torrefied and carbonized at a low temperature. The unprocessed sample and the torrefied samples showed absorption bands at wave numbers in the range 1000–1050 cm⁻¹, while no spectra were observed for the low-temperature carbonized samples. Peaks at wave numbers in the range 700–900 cm⁻¹ indicate aromatic carbons and CH groups [29], and in this zone, it was observed that the absorbance band for the low-temperature carbonized samples increased, while those for the unprocessed sample and the torrefied samples decreased [9]. This result verifies that the chemical structure changed depending on the thermal-treatment temperature. In particular, for the low-temperature carbonized samples, the quantities of aromatic components increased, and therefore, it is assumed that the combustion reactivity was enhanced.

3.3. Non-isothermal thermogravimetric analysis

3.3.1. Combustion reaction zone and characteristics

DTG curves for the torrefied samples and the low-temperature carbonized samples are shown in Fig. 5a and b, respectively. In addition, the DTG curves for samples of coal-blended with the torrefied samples (TW275) and with the low-temperature carbonized samples (CW350) are shown in Fig. 5c and d, respectively. The samples were blended at the co-combustion ratios (torrefied

Table 2a
Effect of temperature on fuel characteristics (fuel ratio and VM).

Sample	Proximate analysis (wt.%, adb)				Fuel ratio	VM (wt.%, daf)
	M	FC	VM	Ash	FC/VM	VM/[(100–(M + Ash))/100]
WC Raw	3.81	7.42	88.72	0.05	0.08	92.28
TW250	3.19	15.51	81.19	0.11	0.19	83.96
TW275	2.90	23.46	73.47	0.17	0.32	75.80
TW300	2.81	29.36	67.58	0.25	0.43	69.71
CW325	3.29	51.57	44.71	0.43	1.15	46.44
CW350	3.40	52.56	43.57	0.47	1.21	45.32
CW375	4.03	61.36	34.13	0.48	1.80	35.74

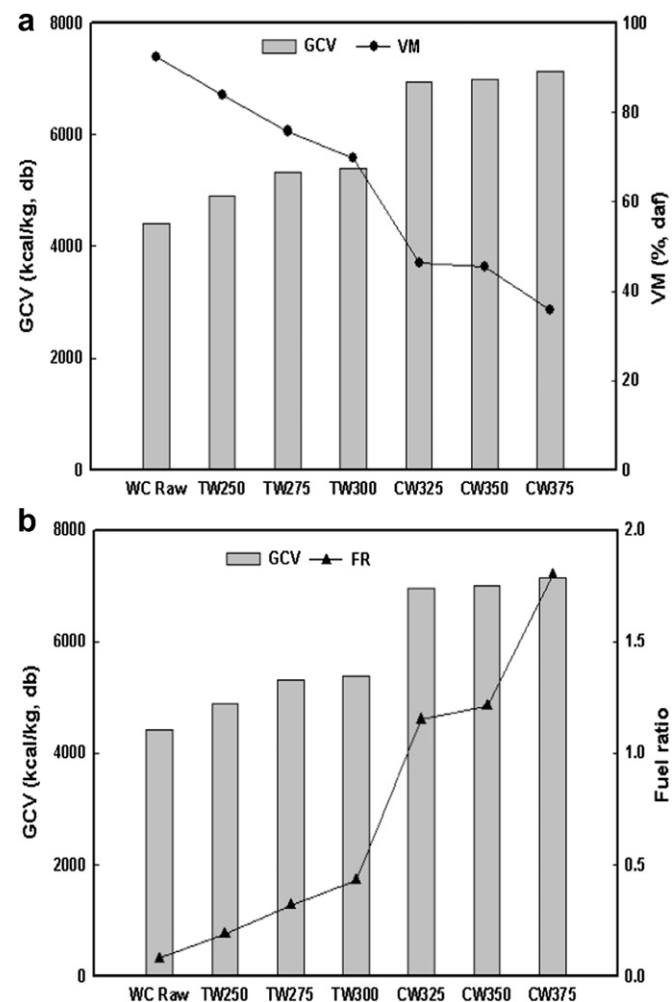


Fig. 2. Variable characteristics of GCV, VM, and FR by torrefaction and low-temperature carbonization: (a) GCV: VM; (b) GCV: FR.

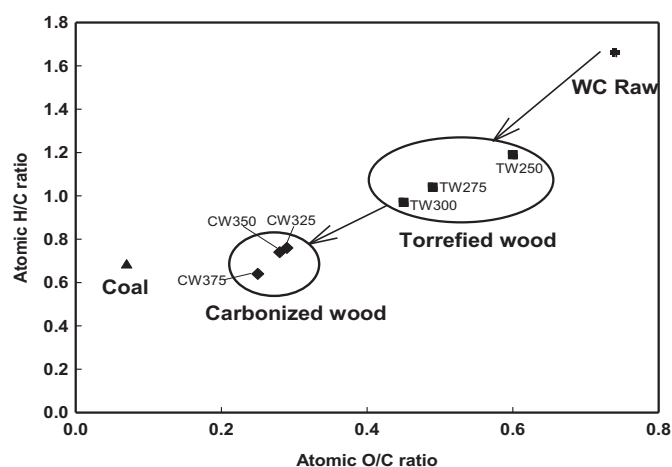


Fig. 3. Van Krevelen diagram for samples prepared at different thermal-treatment temperatures.

samples (TW275) to coal) of 10, 20, and 40% and were denoted 10TW90C, 20TW80C, and 40TW60C, respectively. The low-temperature carbonized samples (CW350) blended with coal were denoted 10CW90C, 20CW80C, and 40CW60C, respectively.

As can be observed in Fig. 5a, both the torrefied samples and the unprocessed sample show two DTG peaks. The feature of the torrefied samples was that they did not show large variations in the peak shape according to the thermal-treatment temperature, except for TW300. However, the second stage showed that as the thermal-treatment temperature was increased, DTG_{max} also increased. This result is very similar to that obtained in a previous study on the torrefaction of woody biomass [6]. This is caused by the removal of volatile components, mainly in hemicellulose and partly in cellulose.

On the other hand, it was observed that the low-temperature carbonized samples showed a single DTG peak, with the exception of CW325, and the DTG curves showed different patterns than those for the unprocessed sample (Fig. 5b), i.e., IT started from a higher temperature and the combustion reaction zone was low. They were also different than the DTG curves for the torrefied samples because of the devolatilization reaction being promoted by the difference in the thermal-treatment temperature. It is assumed that mainly the combustion reactions of the lignin component and char occurred [3,30].

Two DTG peaks were observed at all co-combustion ratios of the coal/TW275 blended samples, and it was found that a lower co-combustion ratio formed the smaller first peak (Fig. 5c). However, in the event that only coal was combusted, it showed a different pattern. This means that the devolatilization reaction occurs much more rapidly in woody biomass than in coal. Therefore, in the event

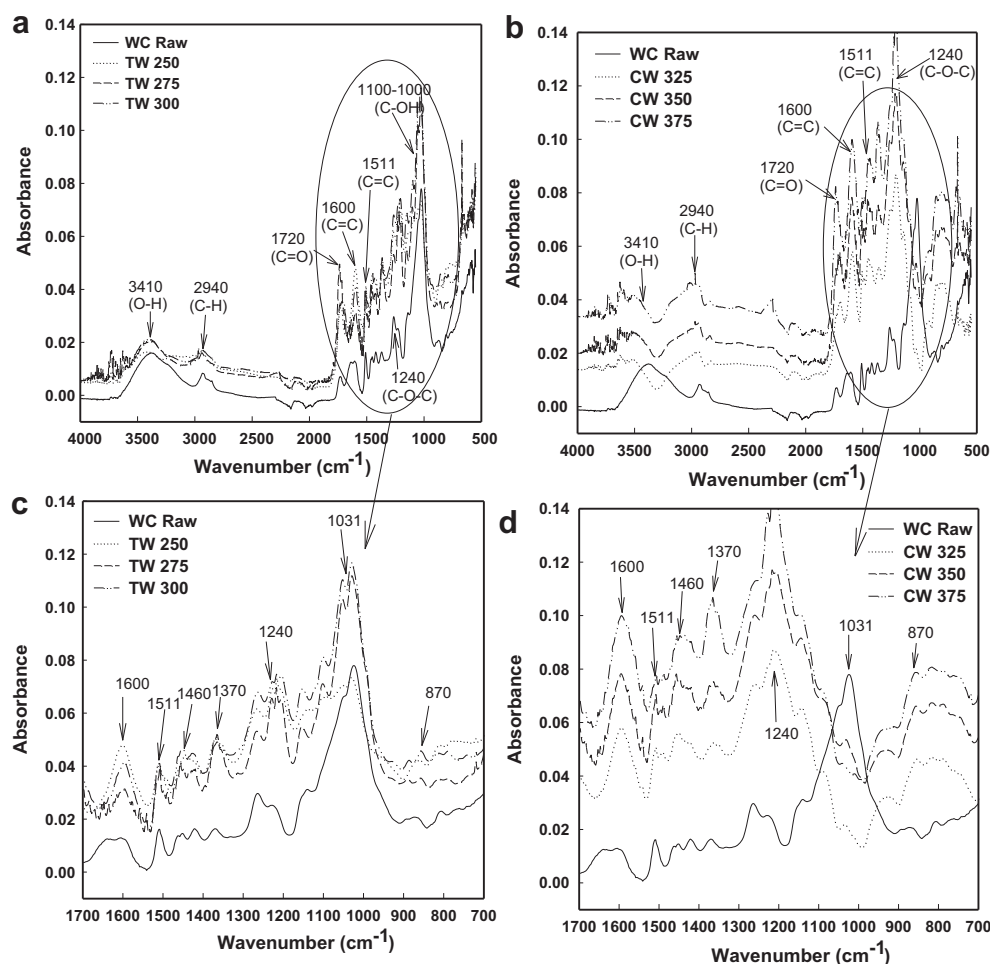


Fig. 4. FT-IR spectra for samples: (a) torrefied wood between 4000 and 500 cm^{-1} ; (b) low-temperature carbonized wood between 4000 and 500 cm^{-1} ; (c) magnification of torrefied wood between 1700 and 700 cm^{-1} ; (d) magnification of low-temperature carbonized wood between 1700 and 700 cm^{-1} .

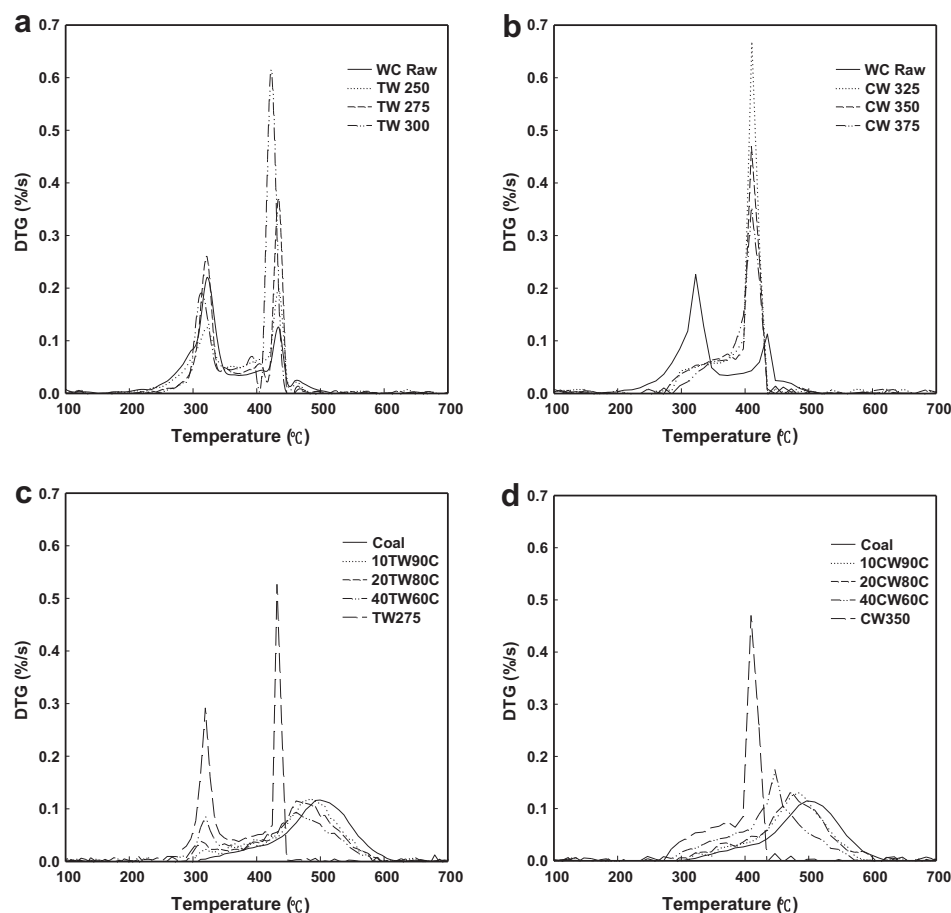


Fig. 5. DTG curves for samples: (a) torrefied wood; (b) low-temperature carbonized wood; (c) TW275/coal blend samples; (d) CW350/coal blend samples.

of single combustion or co-combustion with coal, the fuel input and combustion control should account for pyrolysis, which is the initial reaction during combustion. On the other hand, a single DTG peak was observed at all co-combustion ratios of the coal/CW350 blended samples (Fig. 5d). Among them, the samples with the co-combustion ratios of 10% and 20% showed DTG curves very similar to that for coal. The combustion parameter and weight loss

rate per stage investigated through the DTG curve are listed in Table 3.

According to Table 3, IT for the torrefied samples and the low-temperature carbonized samples was higher than that for the unprocessed sample. The table shows that IT for the sample thermally treated at the highest temperature (CW375) was 292 °C, which was higher by 49–57 °C than that for the unprocessed

Table 3
Characteristic parameters obtained from DTG combustion profiles for raw woody biomass, coal, thermally treated woody biomass and thermally treated woody biomass/coal blend.

Sample		IT (°C)	PT (°C)		DTG _{max} (% s ⁻¹)		BT (°C)	t _q (s)	Weight loss (%)	
			First PT	Second PT	First DTG	Second DTG			First stage	Second stage
Single	Coal	337	—	501	—	0.1168	598	1566	—	85.48
	WC Raw	235	327	433	0.2423	0.1250	487	1512	59.43	30.81
	TW250	243	325	432	0.1193	0.1956	482	1434	41.50	46.06
	TW275	265	320	434	0.2871	0.3679	444	1074	42.86	46.40
	TW300	267	313	422	0.2248	0.6151	438	1026	37.03	56.14
	CW325	276	305	410	0.0565	0.6672	436	960	15.91	77.54
	CW350	277	—	410	—	0.4696	435	948	—	94.68
	CW375	292	—	409	—	0.3509	431	834	—	92.78
Blend	TW275: coal									
	10TW90C	308	319	484	0.0227	0.1237	482	1044	5.61	79.80
	20TW80C	295	319	471	0.0344	0.1164	576	1686	8.48	77.36
	40TW60C	279	320	468	0.0892	0.0980	569	1740	17.37	67.16
	CW350: coal									
	10CW90C	315	—	483	—	0.1314	583	1608	—	86.66
	20CW80C	312	—	478	—	0.1236	570	1548	—	87.12
	40CW60C	297	—	444	—	0.2602	555	1548	—	88.84

TW, torrefied wood; CW, low-temperature carbonized wood; C, coal; t_q, burnout time (BT–IT).

sample (235 °C) and TW250 (243 °C). It is normal that the higher the rank of the coal, the higher the IT [31], so it could be possible that the fuel rank improved as the devolatilization occurred. On the other hand, the table shows that BT dropped more at higher thermal-treatment temperatures, showing the opposite trend to IT. It was found that IT for CW375 was 431 °C, lower than 487 °C for CW375 and 438 °C for TW300.

It was observed that IT for the torrefied/coal blend samples and the low-temperature carbonized/coal blend samples dropped as the co-combustion ratio was increased. This result is in agreement with a study, in which IT for coal or the coal-blended sample decreased linearly as the amount of more reactive coal increased [32]. It showed that IT for the coal-blended samples dropped more because the reactivity of the torrefied samples was higher than that of the low-temperature carbonized samples. In general, the variation in the combustion temperature is caused by the physical and chemical differences in coal [33]. It is caused physically by the size of the particles or the variation in the specific surface area, and chemically by the variation in the bonding structure of carbon. In order to verify this, the specific surface areas of the torrefied samples, low-temperature carbonized samples, and coal were investigated (Table 2). Kastanaki and Vamvuka [14] reported that the biomass char, which was pyrolyzed at 850 °C, had good combustion reactivity resulting from the high porosity due to the pyrolysis.

This work showed that the specific surface areas were $<1.0 \text{ m}^2 \text{ g}^{-1}$ for TW275, $<1.0 \text{ m}^2 \text{ g}^{-1}$ for CW350, and $11.86 \text{ m}^2 \text{ g}^{-1}$ for coal. Moreover, it showed that the specific surface areas for the torrefied samples and the low-temperature carbonized samples were much lower than that for coal. It is thought that the difference in the combustion temperature is caused by variations in the chemical structure rather than physical differences. As shown by the FT-IR spectra results (Fig. 4), it is thought that the chemical structure is determined by the bonding structure of carbon. It was observed that BT dropped as the co-combustion ratio of CW350 to coal was increased (except for a co-combustion ratio of 10%). Conversely, it was observed that BT increased for the co-combustion ratios of 20% (20TW80C) and 40% (40TW60C) for TW275.

The burnout time for the torrefied samples was shorter than that for coal, with that for coal at 1566 s and for TW275 at 1074 s. However, the burnout times for TW275 with co-combustion ratios of 20% and 40% increased to 1686 s and 1740 s, respectively.

In previous studies in which BT for blended coal had no weighted average properties [15,32], and when two different peaks were observed, the combustion of each component occurred independently [34], and its burnout time increased. For the low-temperature carbonized samples, the burnout time decreased as the co-combustion ratio was increased, except in the case in which it increased to 1608 s when the co-combustion ratio was 10%. This result implies that in the event of co-combustion with coal, the combustion characteristics may vary depending on the thermal-treatment temperature and blend ratio.

3.3.2. Kinetic parameters

As listed in Table 4, the value of E for the unprocessed sample was $23.79 \text{ kcal mol}^{-1}$ in the first stage and $12.62 \text{ kcal mol}^{-1}$ in the second stage. Compared with $29.28 \text{ kcal mol}^{-1}$ and $3.65 \text{ kcal mol}^{-1}$, which were the results obtained by Yorulmaz and Atimatay [20], and $28.42 \text{ kcal mol}^{-1}$ and $34.63 \text{ kcal mol}^{-1}$, which were the results obtained by Shen et al. [22], the first stage showed lower values and the second showed intermediate values.

The activation energy for the torrefied samples was in the range $20.91\text{--}23.03 \text{ kcal mol}^{-1}$ in the first stage and $11.58\text{--}14.35 \text{ kcal mol}^{-1}$ in the second stage, and no large variation from that for the unprocessed sample was observed. The activation energy for the low-temperature carbonized samples was in the range $30.79\text{--}34.62 \text{ kcal mol}^{-1}$ in the second stage, which was less than $43.48 \text{ kcal mol}^{-1}$ for coal and close to $34.70 \text{ kcal mol}^{-1}$ for wood char thermally treated at 850 °C [14].

The value of E is greater in the devolatilization stage, which is the first stage of torrefaction, compared to the char combustion stage; hence, it is necessary to pay attention to the initial combustion characteristics at the time of co-combustion of biomass blended with coal. On the contrary, in the case of the low-temperature carbonized sample, the number of DTG peaks is the same as in the case of coal and the value of E is low. Therefore, we can expect the combustion reaction to be expedited at the time of co-combustion.

The pre-exponential factor for the torrefied samples was $16.00\text{--}17.95$ in the first stage and $7.49\text{--}9.77$ in the second stage, which showed that the pre-exponential factor in the first stage was greater than that in the second stage. It decreased in the first stage and increased in the second stage, compared to the pre-exponential factor for the unprocessed sample. On the other hand, the pre-

Table 4
Thermal kinetic results of all samples.

Sample		First stage					Second stage				
		OM	Temp. interval (°C)	E (kcal mol ⁻¹)	$\ln A$ (s ⁻¹)	R^2	OM	Temp. interval (°C)	E (kcal mol ⁻¹)	$\ln A$ (s ⁻¹)	R^2
Single	Coal	—	—	—	—	—	D3	337–598	43.48	25.80	0.9620
	WC Raw	D1	235–370	23.79	18.69	0.9746	D4	370–487	12.62	7.06	0.9616
	TW250	D1	243–361	22.32	16.96	0.9845	D1	361–482	11.96	7.86	0.9621
	TW275	R2	265–364	20.91	16.00	0.9513	D1	364–444	11.58	7.49	0.8891
	TW300	R2	267–346	23.03	17.95	0.9608	D1	346–438	14.35	9.77	0.9048
	CW325	R2	276–340	14.60	9.85	0.9908	D1	340–436	32.62	23.65	0.9546
	CW350	—	—	—	—	—	D1	277–435	30.79	22.44	0.9908
	CW375	—	—	—	—	—	D1	292–431	34.62	25.35	0.9838
	CW375	—	—	—	—	—	D1	292–431	34.62	25.35	0.9838
Blend	TW275: coal	—	—	—	—	—	—	—	—	—	—
	10TW90C	O3	308–355	1.82	−0.47	0.9993	D3	355–582	30.45	17.71	0.9896
	20TW80C	O3	295–351	2.52	0.50	0.9908	D3	351–576	27.39	15.86	0.9887
	40TW60C	R2	279–353	19.16	13.67	0.9677	D3	353–569	20.73	11.60	0.9874
	CW350: coal	—	—	—	—	—	—	—	—	—	—
	10CW90C	—	—	—	—	—	D3	315–583	34.90	20.74	0.9940
	20CW80C	—	—	—	—	—	D3	312–570	32.64	19.49	0.9968
	40CW60C	—	—	—	—	—	D3	297–555	30.14	18.54	0.9918
	40CW60C	—	—	—	—	—	D3	297–555	30.14	18.54	0.9918

E , Activation energy; A , pre-exponential factor; R , correlation coefficient of linear regression; OM, the form of $g(\alpha)$ that gives a straight line with the highest correlation coefficient will be considered the function of the model that best represents the kinetics of mass loss for each separate reaction.

exponential factor for the low-temperature carbonized samples was 22.44–25.35, which is similar to that for coal, i.e., 25.80.

For the samples blended with coal, it was found that the activation energy for the torrefied samples increased in the first stage and decreased in the second stage as the co-combustion ratio was increased. In particular, at a co-combustion ratio of 40%, it was 19.16 kcal mol⁻¹ in the first stage and 20.73 kcal mol⁻¹ in the second stage; thus, this verified that torrefied samples and coal each combusted independently. Meanwhile, the value of E over the co-combustion ratios for the low-temperature carbonized samples to coal lay in the range 30.14–34.90 kcal mol⁻¹. However, this result is lower in value than the weighted average value of 43.48 kcal mol⁻¹ for coal and 30.79 kcal mol⁻¹ for CW350. It can be inferred from this result that the combustion reactivity was promoted as the chemical structure was changed by thermal treatment, as explained above. Consequently, we confirmed that the values of E and A in the samples with blended CW350 and coal decreased as the blend ratio increased. I also confirmed that as a result, the combustion rate (da/dt) became higher owing to an increased value of the constant (k), which represents the reaction rate. However, in the case of the sample torrefied at 275 °C, I confirmed that the combustion rate was not the same, according to the co-combustion ratio, because of an opposite tendency shown in the devolatilization and char combustion stages.

The combustion reaction mechanism for the unprocessed sample was D1, which is a one-dimensional diffusion mechanism with deceleration curves in the first stage, but it showed a D4 mechanism in the second stage. However, as the thermal-treatment temperature increased, it changed to R2 in the first stage and to D1 in the second stage.

For all coal samples and TW275 blended co-combustion ratios, the combustion mechanisms were O3 and R2 in the first stage and D3 in the second stage. On the other hand, for all low-temperature carbonized samples (CW350) and coal-blended co-combustion ratios, the combustion reaction mechanism O3 showed the highest correlation coefficient; therefore, it was verified that this is a suitable model. In order to conduct co-combustion with blended coal and thermal-treated biomass in the future, it is necessary to deduce the parameters necessary for combustion control after studying the combustion characteristics and combustion reaction rate.

4. Conclusions

The fuel characteristics of samples to which a torrefaction and low-temperature carbonization were applied as a preprocessing for woody biomass are shown as follows.

1. For the energy balance, it was shown that the energy yield was higher with the torrefied material, and for the fuel characteristics, it was found that the low-temperature carbonized samples were nearest to those of coal.
2. For the combustion characteristics, the low-temperature carbonized samples showed DTG curves that were more similar to those shown by coal than those shown by the torrefied samples. Furthermore, in the event of blending with coal, two types of independent combustions were observed for the coal/torrefied samples blend but only a single type of combustion was observed for the coal/low-temperature carbonized sample blend.
3. In the case of samples blended with coal and low-temperature carbonized samples at 350 °C, it was confirmed that the activation energy and all index parameters decreased as the blend ratio increased. It was also confirmed that as a result, the combustion rate (da/dt) became higher owing to an increased value of the constant (k), which represents the reaction rate.

However, in the case of the sample torrefied at 275 °C, it was confirmed that the combustion rate was not the same, according to the co-combustion ratio, because of an opposite tendency shown in the devolatilization and char combustion stages.

4. It was confirmed that the combustion rate increased when the thermal-treated samples were blended, compared to single combustion of coal. However, in the case of torrefied samples, it is necessary to pay attention to combustion control at the time of co-combustion, because the torrefied samples show two DTG peaks.

As the result, it was verified that the fuel characteristics varied depending on the thermal-treatment temperature and consequently the combustion characteristics varied.

References

- [1] Biagini E, Cioni M, Tognotti L. Development and characterization of a lab-scale entrained flow reactor for testing biomass fuels. *Fuel* 2005;84(12, 13): 1524–34.
- [2] Gurgel VCA, Saastamoinen J, Carvalho Jr JA, Aho M. Over lapping of the devolatilization and char combustion stages in the burning of solid fuel particles. *Combustion and Flame* 1999;116(4):567–79.
- [3] Park SW, Jang CH. Effects of pyrolysis temperature on changes in fuel characteristics of biomass char. *Energy* 2012;39(1):187–95.
- [4] Bergman PCA, Boersma AR, Zwart RWR, Kiel JHA. Torrefaction for biomass co-firing in existing coal-fired power stations “BIOCOAL”. Energy Research Centre of the Netherlands (ECN); 2005.
- [5] Prins MJ, Ptasiński KJ, Janssen FJJG. Torrefaction of wood. Part 2. Analysis of products. *Journal of Analytical and Applied Pyrolysis* 2006;77(1): 35–40.
- [6] Arias B, Pevida C, Feroso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing Technology* 2008;89(2):169–75.
- [7] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology* 2011;102(2): 1246–53.
- [8] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* 2008;87(6):844–56.
- [9] Rousset P, Aguiar C, Labbe N, Commandre JM. Enhancing the combustible properties of bamboo by torrefaction. *Bioresource Technology* 2011;102(17): 8225–31.
- [10] Chen WH, Hsu HC, Lu KM, Lee WJ, Lin TC. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. *Energy* 2011;36(5):3012–21.
- [11] Chouchene A, Jeguirim M, Khiari B, Trouvé G, Zagrouba F. Study on the emission mechanism during devolatilization/char oxidation and direct oxidation of olive solid waste in a fixed bed reactor. *Journal of Analytical and Applied Pyrolysis* 2010;87(1):168–74.
- [12] Sahu SG, Sarkar P, Chakraborty N, Adak AK. Thermogravimetric assessment of combustion characteristics of blends of a coal with different biomass chars. *Fuel Processing Technology* 2010;91(3):369–78.
- [13] Abdullah H, Wu H. Biochar as a fuel: 1. Properties and grindability of biochars produced from the pyrolysis of mallee wood under slow-heating conditions. *Energy Fuels* 2009;23(8):4174–81.
- [14] Kastanaki E, Vamvuka D. A comparative reactivity and kinetic study on the combustion of coal-biomass char blends. *Fuel* 2006;85(9):1186–93.
- [15] Vamvuka D, Sfakiotakis S. Combustion behaviour of biomass fuels and their blends with lignite. *Thermochimica Acta* 2011;526(1, 2):192–9.
- [16] Yuan JH, Xu RK, Zhang H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresource Technol* 2011;102(3): 3488–97.
- [17] ASTM D 3172. Standard practice for proximate analysis sample of coal and coke.
- [18] ASTM D 3174. Standard test method for ash in the analysis sample of coal and coke.
- [19] ASTM D 3175. Standard test method for volatile matter in the analysis sample of coal and coke.
- [20] Yorulmaz SY, Atimtay AT. Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis. *Fuel Processing Technology* 2009;90(7–8):939–46.
- [21] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature* 1964;201:68–9.
- [22] Shen DK, Gu S, Luo KH, Bridgwater AV, Fang MX. Kinetic study on thermal decomposition of woods in oxidative environment. *Fuel* 2009;88(6):1024–30.
- [23] Doyle CD. Kinetic analysis of thermogravimetric data. *Journal of Applied Polymer Science* 1961;5(15):285–92.

- [24] Irfan MF, Arami-Niya A, Chakrabarti MH, Mohd W, Daud AW, Usman MR. Kinetics of gasification of coal, biomass and their blends in air (N_2/O_2) and different oxy-fuel (O_2/CO_2) atmospheres. *Energy* 2012;37(1):665–72.
- [25] Guo J, Lua AC. Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model. *Biomass and Bioenergy* 2001;20(3): 223–33.
- [26] Sjöström E. In: *Wood chemistry: fundamentals and applications*. 2nd ed. San Diego: Academic Press; 1993.
- [27] Prins MJ, Ptasiński KJ, Janssen FJJG. More efficient biomass gasification via torrefaction. *Energy* 2006;31(15):3458–70.
- [28] Sevilla M, Maciá-Agulló JA, Fuertes AB. Hydrothermal carbonization of biomass as a route for the sequestration of CO_2 : chemical and structural properties of the carbonized products. *Biomass and Bioenergy* 2011;35(7): 3152–9.
- [29] Evans PA. Differentiating “hard” from “soft” woods using Fourier transform infrared and Fourier transform Raman spectroscopy. *Spectrochimica Acta Part A* 1991;47(9, 10):1141–7.
- [30] Kim DW, Lee JM, Kim JS, Seon PK. Study on the combustion characteristics of wood-pellet and Korean anthracite using TGA. *Korean Chemical Engineering Research* 2010;48(1):58–67.
- [31] Carpenter AM. Coal blending for power stations. IEACR/81. London, UK: IEA Coal Research; 1995.
- [32] Artos V, Scaroni AW. T.g.a. and drop-tube reactor studies of the combustion of coal blends. *Fuel* 1993;72(7):927–33.
- [33] Lee SH, Shon EK. Effect of molten caustic leaching on the combustion characteristics of anthracite. *Fuel* 1997;76(3):241–6.
- [34] Cumming JW. A DTG combustion study on anthracitic and other coal chars. *Thermochimica Acta* 1989;155:151–61.